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LUMINESCENT GLASS AS A PROMISING MATERIAL FOR X-RAY CONVERSION IN RADIATION INTROSCOPES

O. V. Kaz'mina,[1] A. N. Abiyaka,[1] and Yu. A. Moskalev[1]

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Terbium oxide activated $Li_2O - BaO - SiO_2$ and $Al_2O_3 - B_2O_3 - SiO_2$ glasses have been developed. These glasses have a relatively high light output and can be used for x-ray conversion in radiation introscopes. A method for measuring the brightness of x-ray luminescence converters using the equipment base of radiation introscopes has been developed.

Quite a large number of luminescent materials which can be used as radiation detectors or converters in a wide energy range are now known. However, not all materials meet the following requirements for the use of x-rays in introscopes:

high absorption of the working beam of ionizing radiation;

high spatial resolution;

matching of the luminescence spectrum with the spectral characteristic of the CCD array or photodetector of the introscope; and,

technological possibility of manufacturing a converter in the form of a large-area screen.

Inorganic glass can be used as an x-ray converter [2]. Because of its unique properties, such as transparency in the visible range of the spectrum, adequate strength, resistance to external media, and flexible manufacturability, which makes it possible to fabricate parts with different shapes by relatively simple means, glass is widely used for manufacturing the structural members of various types of devices and measuring apparatus.

Even though glass has all these advantages over other materials, glass-based x-ray converters are not manufactured in Russia. The company Collimated Holes, Inc. (USA) manufactures x-ray luminescent glasses but the glass composition which this company has developed has not been published in the technical literature.

The aim of the present work is to develop luminescent-glass compositions which are suitable for screen converters of x-ray radiation which are used in industrial radiography and introscopy.

According to Weyl's classification, glasses which are capable of luminescing fall into three groups depending on the state of the luminescence activators. Activators belonging to the first group are neutral molecules which are distributed in the glass and do not interact with one another or with the solvent molecules surrounding them. These activators can re-emit in the form of photoluminescence the energy which they have absorbed from the outside the glass. An example is glass activated by cadmium sulfide. The luminescence of glasses which belong to the second group is due to a transition of the activators into an atomic state. Examples are lead, antimony, bismuth, and other elements. The activators present in an atomically dispersed state in the glass can luminesce under appropriate conditions. The glass matrix isolates the centers of luminescence and does not participate in their formation. The third and largest group contains glasses whose centers of luminescence are ions which participate in the formation of the structure of the glass, for example, glass with elements whose valence can change. The luminescence spectra of individual elements depend on the composition of the glass and the conditions under which it was obtained.

The existing methods for measuring the brightness of the x-ray luminescence of various materials are based on a general scheme which includes a source of radiation, the experimental sample, and a detector which detects the light flux due to x-ray luminescence and is combined with the measuring apparatus. X-ray apparatus with energy in the range 20 – 200 kV or isotopic sources of γ-rays, such as ^{75}Se and ^{241}Am, with γ-ray energies 20 – 300 keV are used as radiation sources.

Different detectors — luminescence meters — are used depending on the intensity of the radiation source and the brightness of the x-ray luminescence. For example, photomultipliers (PMs) operating in the counting mode are used in the case of isotopic sources. When x-ray apparatus is used the brightness of the radiation from the samples is measured

[1] Tomsk Polytechnic University, Tomsk, Russia.

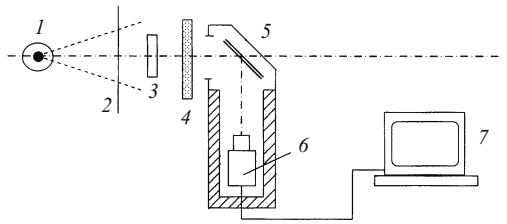

Fig. 1. Scheme for measuring the brightness of x-ray luminescence: *1*) radiation source — x-ray apparatus; *2*) x-ray radiation filter; *3*) experimental sample of luminescent glass; *4*) protective glass; *5*) x-ray sensitive unit of the introscope; *6*) CCD array; *7*) computer.

with PMs operating in the tone mode or with selenium photocells combined with a galvanometer.

The spectral compatibility of the luminescence spectra of the glass of interest (the maximum wavelength of the x-ray luminescence spectrum is 550 nm) and the CCD array of the introscope must be taken into account in order to determine the suitability of the luminescing glasses as radiation converters in introscopes. The ISD-017 AP CCD camera of a RIN-120 introscope with the array operating in the light-signal accumulation mode served as the measuring device. A RUP-150/300 x-ray apparatus was used as the radiation source. The measurement scheme is displayed in Fig. 1.

This method of measurement automatically solves the question of the spectral compatibility of the x-ray luminescence of glasses and the sensitivity of the CCD array. Signal accumulation on the array increases the accuracy of the measurements. Using the "Diada" software, measurements were performed on several samples of glasses simultaneously and their brightness was compared with a reference standard.

Measurements were performed on powders of the obtained glasses with fractions 0.315 – 0.15 mm in the following regime of the x-ray apparatus: accelerating voltage 220 kV and current strength 6 mA. An x-ray filter, consisting of a 1.5 mm thick steel plate, was used to obtain the soft component of the radiation (< 50 keV).

Previous investigations performed on lead-containing glasses using rare-earth elements (REEs) as x-ray luminescence activators showed that glass activated with 10% terbium has the highest luminescence intensity. For this reason subsequent studies were performed using this activator [3].

Even though it is relatively easy to make lead-containing glass, making glasses with the compositions studied and with prescribed properties entailed difficulties, such as a high nonuniformity of the glass mass and the presence of hidden liquation (metastable liquation) [4], which ultimately makes it more difficult to obtain a prescribed glass structure.

For this reason, scintillating glasses belonging to the systems Li_2O – BaO – SiO_2 and Al_2O_3 – B_2O_3 – SiO_2 were considered for the base arrays (See Table 1). According to the data in [5], the technical scintillation efficiency of these glasses, activated by cerium oxide, under excitation by γ rays is 2 – 3% with respect to a NaI(Tl) crystal.

To decrease the negative effect of impurities on the luminescence properties of the glass, batches were synthesized from chemically-pure grade reagents with 10% terbium (above 100%) introduced. The glass was made in 200 ml corundum crucibles in an electric furnace with silicon carbide heating elements at temperature 1350°C and then annealed in a crucible.

As one can see from the data in Table 1, the initial glass composition (No. 1), corresponding to grade Z-56-8, was varied by adding compounds chosen on the basis of their effect on the oxidation – reduction reactions in the glass mass and the changes occurring in certain properties of the glass, specifically, its density.

Since only the Tb^{3+} ion has the capability of luminescing and terbium can exist in the tri- and tetravalent forms, between which Tb^{3+} : Tb^{4+} equilibrium is established, carbon was introduced into the glass (No. 2) in order to shift the reaction in the direction of the formation of trivalent terbium. To increase the glass density and, correspondingly, its absorbing power, a heavy element in the form of tungsten oxide was introduced into the glass (No. 4). In addition, glass compositions where barium oxide was partially replaced with magnesium oxide were tested (Nos. 3 and 5). The results of

TABLE 1

Glass No.	Mass content, %							Additional additives (above 100%), %			
	B_2O_3	SiO_2	Li_2O	BaO	MgO	Al_2O_3	Na_2O	WO_3	NH_4F	C	GdO
1	7.29	64.81	9.68	18.21	–	–	–	–	2	–	–
2	7.29	64.81	9.68	18.21	–	–	–	–	–	2	–
3	7.29	64.81	9.68	14.57	3.64	–	–	–	2	–	–
4	7.29	64.81	9.68	18.21	–	–	–	20	–	–	–
5	7.29	64.81	9.68	14.57	3.64	–	–	–	–	–	–
6	7.29	64.81	9.68	14.57	3.64	–	–	–	–	–	5
7	34.08	39.17	–	–	–	16.64	10.11	–	–	–	–
8	34.08	39.17	–	–	–	16.64	10.11	–	–	–	5

our investigations of the luminescence intensity of the experimental compositions are presented in Fig. 2.

Evidently, the luminescence intensity of the glass powder with the base composition (sample No. 1) increases when carbon is introduced in amounts up to 2000 arb. units. Adding tungsten oxide to the glass increases the luminescence intensity only negligibly up to 1100 arb. units as compared with the 800 arb. units for the base composition.

The composition where magnesium oxide replaces 20% of the barium oxide exhibits the highest luminosity (4000 arb. units). An increase in the luminescence of glass with magnesium was also noted in [6], where it was established that a partial substitution of magnesium oxide for barium oxide in amounts 5 – 10% (molar content) increases the relative scintillation efficiency of alkali-free fluorine-containing glasses, and the luminescence yield of the composition with magnesium and ammonium fluoride (No. 3) is negligible, only 1300 arb. units.

There exist data showing that the interaction of REEs with one another affects the luminescence characteristics of a material. For comparatively low concentrations the interaction is expressed mainly in a transfer of energy from one REE to another, as a result of which quenching of one or both interacting ions, quenching of one and its sensitization of another REE, or only sensitization of another REE is observed. Other indications of an interaction can also be observed at high concentrations: a change in the absorption and luminescence spectra. Experimental data on the sensitizing influence of dysprosium, cerium, and gadolinium on terbium in inorganic glass are presented in [7]. For this reason a composition (No. 6) into which 5% gadolinium oxide was introduced was also tested. The luminescence intensity was 3000 arb. units, which is greater than for the base composition but less than for the most strongly luminescing composition (No. 5) with the magnesium replacing barium.

For the $Al_2O_3 – B_2O_3 – SiO_2$ glass (No. 7), modified with cadmium oxide, an increase of the luminescence intensity from 1600 to 2000 arb. units is also observed when two REEs are used simultaneously.

It is evident that when gadolinium and terbium are present simultaneously in the glasses with the compositions studied a transfer of the energy at which the activator is sensitized occurs.

When using glass as an x-ray converter its technological characteristics must be taken into account. Some of them can be predicted on the basis of the phase diagram of the system to which the glass composition of interest belongs. The compositions considered for the $Li_2O – BaO – SiO_2$ and $Al_2O_3 – B_2O_3 – SiO_2$ glasses, in contrast to lead-containing glasses, do not have metastable liquation and exhibit only a weak tendency toward crystallization; this is due to the low melting temperature and the fact that the compositions lie near eutectic points [8].

In summary, the intensity of x-ray luminescence of glass depends not only on the type and concentration of the activator but also on the base composition of the glass. The luminescence can be increased by introducing additional modifying agents to change the base composition of the glass.

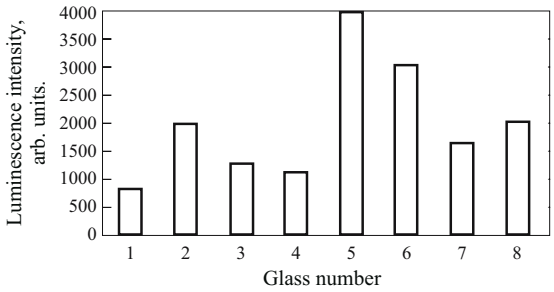

Fig. 2. Luminescence intensity of glass powders with different compositions (accelerating voltage 120 kV, current strength 3 mA, exposure 4 sec).

As a result of its transparency in the visible region of the spectrum, adequate strength, flexible manufacturability, and relatively high light output, inorganic glass with the compositions developed can be used as x-ray converters in introscopes.

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